

## Facile Surfactant-Free Preparation, Characterization and Investigation of Optical Properties of Zirconia Nanostructures

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(Received 19 March 2015; published online 22 August 2015)

Zirconia nanostructures have been successfully synthesized through sonochemical-assisted route. Zirconia nanostructures were synthesized by employing of the zirconyl nitrate and tetramethylethylenediamine (TMED) as starting materials. Here, TMED was used not only as precipitator, but also as capping agent to form zirconia nanostructures. The products were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), ultraviolet–visible (UV–vis) spectroscopy and scanning electron microscopy (SEM). The obtained results demonstrated that utilizing of this precipitator is suitable choice for preparation of zirconia nanostructures with very uniform sphere-like morphology.

**Keywords:** Zirconia, Nanostructures, Optical properties.

PACS numbers: 81.07. – b, 78.67. – n

### 1. INTRODUCTION

The preparation of nanomaterials has attracted broad scientific attention due to their useful applications in various areas during the last decades [1,2]. Among these nano-scale materials, zirconia as an important metal oxide has been attracted significant scientific and industrial interest for a long time because of its specific optical and electrical properties as well as potential applications, including transparent optical devices and electrochemical capacitor electrodes, fuel cells and catalysts.  $ZrO_2$  has three crystal forms that are stabilized at different temperature ranges: monoclinic (below 1170 °C), tetragonal (1170–2370 °C), and cubic (2370–2680 °C). Up to now, several methods have been developed to synthesize zirconia, such as sol–gel, hydrothermal, thermal decomposition, microwave irradiation, precipitation, and sonochemical [3-6]. Recently, the ultrasonic route as a fast, convenient, and economical method has been widely utilized to prepare new nanostructured materials. Ultrasonic irradiations bring about cavitation in a liquid medium where the formation, growth and implosive collapse of bubbles take place. The collapse of bubbles with short lifetimes (less than a nanosecond) generates intense local heating and we report synthesis of zirconia nanostructures via surfactant-free sonochemical-assisted route by employing zirconyl nitrate and tetramethylethylenediamine (TMED).

### 2. MATERIALS AND METHOD

All the chemical reagents used in our experiments were of analytical grade and were used as received without further purification. Zirconyl nitrate, tetramethylethylenediamine (TMED), liquor ammonia solution containing 25% ammonia were obtained from Merck Co. Distilled water was used for all the experiments. A multiwave ultrasonic generator (Sonicator 3000; Bandeline, MS 72, Germany), equipped with a converter/transducer and titanium oscillator (horn),

12.5 mm in diameter, operating at 20 kHz with a maximum power output of 80 W, was used for the ultrasonic irradiation. Fourier transform infrared (FT-IR) spectra were recorded on Varian 4300 spectrophotometer in KBr pellets. Powder X-ray diffraction (XRD) patterns were collected from a diffractometer of Philips Company with X'PertPro monochromatized Cu K $\alpha$  radiation ( $k = 1.54 \text{ \AA}$ ). Microscopic morphology of products was visualized by a Hitachi s4160 Japan scanning electron microscope (SEM). The electronic spectra of the zirconia were obtained on a Scinco UV–vis scanning spectrometer (Model S-4100). To prepare the zirconia nanostructures, 1 mmol of TMED was dissolved in 40 mL of distilled water and then, added into a solution of ZN (1 mmol of ZN dissolved in 40 mL of distilled water) drop-wise under ultrasound irradiation. The white gel-like product obtained was filtered and washed repeatedly with distilled water. The final product was dried at 80 °C and calcined at 600 °C for 4 h. To study the effect of TMED on the morphology of the zirconia nanostructures, one experiment was carried out by  $NH_4OH$  instead of TMED (blank test). In the blank test 1, 8 mmol of ammonia dissolved in 50 mL distilled water and was added into a solution including 1 mmol of ZN dissolved in 40 mL of distilled water (Table 1). The as-prepared nanostructures were characterized by (SEM), (UV–vis) spectroscopy, (FT-IR) and (XRD) techniques.

**Table 1** – Preparation conditions for samples.

Sample No	Ultrasonic irradiation	Morphology
1	TMED	Homogeneous sponge-like
2 <sup>a</sup>	$NH_4OH$	Agglomerated particle-like

<sup>a</sup> Blank test, in the absence of TMED.

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### 3. RESULTS AND DISCUSSION

In the present study, zirconia nanostructures were prepared by using zirconyl nitrate and TMED as starting reagents via a surfactant-free sonochemical-assisted route.

The XRD pattern of the sample 1 has been shown in Fig. 1. All of the diffraction peaks of the product in Fig. 1 can be indexed to tetragonal zirconium dioxide (space group P42/nmc, JCPDS card 88-1007). The average crystal size of the as-prepared product was calculated from Debye-Scherrer formula [7] given by the following formula:

$$\tau = k\lambda/\beta\cos\theta \quad (1)$$

where,  $\tau$  is the crystal size,  $\beta$  is the breadth of the observed diffraction line at its half intensity maximum,  $k$  is the so-called shape factor and  $\lambda$  is the wavelength of X-ray source used in XRD. The average crystal size of the as-prepared product was about 15 nm.

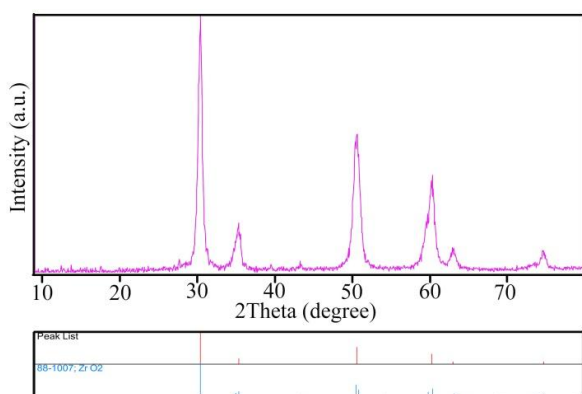


Fig. 1 – XRD patterns of sample 1.

Fig. 2a and 2b show FT-IR spectra of sample 1 after washing steps and after calcination, respectively. The weak (C-N) stretching vibration band at  $1340\text{ cm}^{-1}$  and (C-H) bending vibration band  $1382\text{ cm}^{-1}$  indicates the presence of TMED in the pores after washing steps (Fig. 2a). They completely disappear after calcination at  $600^\circ\text{C}$ . The absorption band centered at  $3447\text{ cm}^{-1}$  and a weak peak at  $1631\text{ cm}^{-1}$  are ascribed to the  $\nu(\text{OH})$  stretching and bending vibrations, respectively, which indicates the presence of physisorbed water molecules linked to zirconium dioxide sample.

SEM images of the samples 1 and 2 have been shown in Fig. 3a and 3b. As seen in Fig. 3a, by using of the TMED, homogeneous sponge-like zirconia nanostructures obtained. In the absence of TMED, the particles coalesced and turn into agglomerated particle-like structures. It seems that when TMED utilized as precipitator (Fig. 3a), the chance of collision between  $\text{ZrO}(\text{OH})_2$  nanoparticles decreased because of steric hindrance effect of TMED, and therefore homogeneous sponge-like zirconia nanostructures formed. The bifunctional TMED can act as both precipitator for  $\text{ZrO}(\text{NO}_3)_2$  to  $\text{ZrO}(\text{OH})_2$  and capping agent for the  $\text{ZrO}(\text{OH})_2$  nanoparticles by hindering the aggregation of nanoparticles.

The optical characteristics of the zirconia nanostructures with sphere-like morphology were examined by UV-vis absorbance analysis. Fig. 3a shows the UV-vis absorbance spectrum of the sample 1.

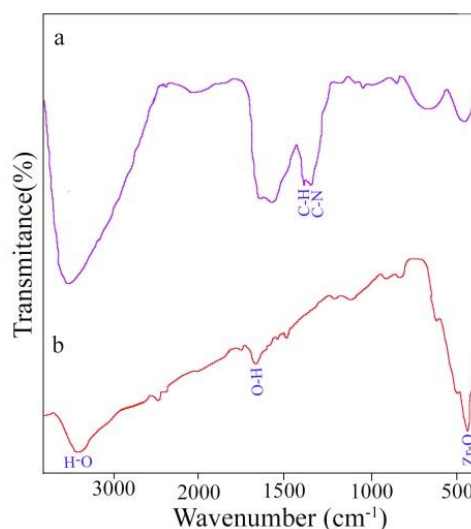


Fig. 2 – FT-IR spectra of sample 1 after washing (a), and after calcination (b).

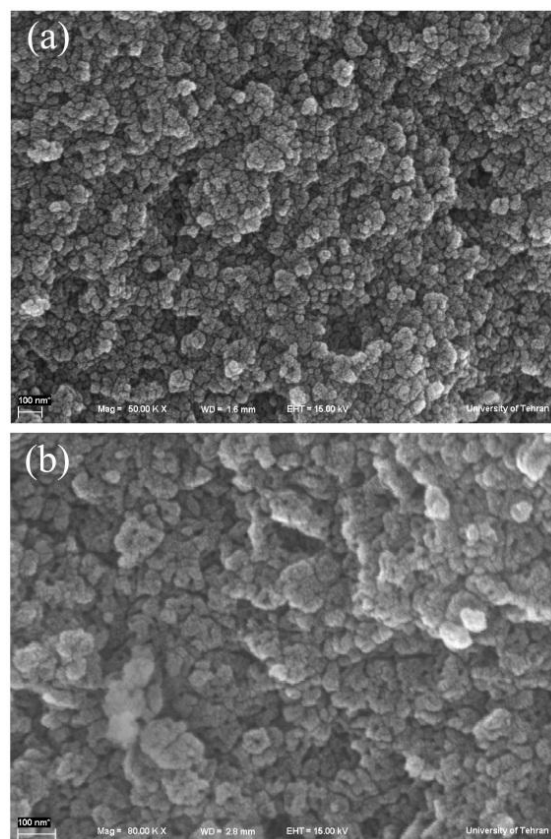
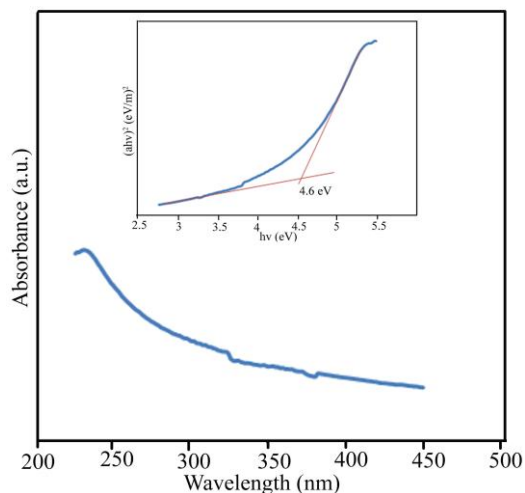


Fig. 3 – SEM images of (a) sample 1, (b) sample 2.

The nanostructures show the absorption spectrum with an absorption band at  $226\text{ nm}$ . Utilizing Tauc's formula, the band gap can be obtained from the absorption data. The energy gap ( $E_g$ ) of the as-obtained zirconia has been calculated by extrapolating the linear portion of the plot of  $(ah\nu)^2$  against  $h\nu$  to the energy axis (Fig. 4). The  $E_g$  value of the zirconia nanostructures (sample 1) is calculated to be  $4.6\text{ eV}$ , which has a red shift of about  $0.4\text{ eV}$  compared with the band gap value of bulk zirconium dioxide ( $5\text{ eV}$ ). The red shift of the absorption band can be originated from the various

structural defects [8]. The obtained data are in good agreement with previous report [9].



**Fig. 4** – UV-vis absorbance spectrum of the sample 1 (inset: the curve of  $(ahv)^2$  against  $hv$ ).

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## 4. CONCLUSIONS

Shortly, homogeneous sponge-like zirconia nanostructures were successfully prepared by using zirconyl nitrate and tetramethylethylenediamine as starting agents in the presence of ultrasound irradiation. Here, TMED was used not only as precipitator, but also as capping agent to form zirconia nanostructures. Here, TMED was used not only as precipitator, but also as capping agent to form zirconia nanostructures. High purity of the as-obtained zirconia nanostructures was confirmed by XRD and FT-IR analyses. The optical characteristics of the obtained zirconia nanostructures were also examined.

## ACKNOWLEDGEMENTS

Authors are grateful to the council of Council of University of Kashan on this work by Grant number (22134324/45).